

# 2006 R&D 100 AWARDS ENTRY FORM

## 1 Submitting Organization

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AFFIRMATION: I affirm that all information submitted as a part of, or supplemental to, this entry is a fair and accurate representation of this product.

Submitter's signature: \_\_\_\_\_

## 2 Joint entry with: Not applicable

## 3 Product name:

**High-Efficiency Multiband Semiconductor Material for Solar Cells**

## 4 Briefly describe (25 words or less) what the entry is (e.g. balance, camera, nuclear assay, etc.)

A novel semiconductor material with multiple, tunable band gaps for use in high efficiency, single-junction, full-spectrum solar cells.

## 5 When was this product first marketed or available for order? (Must have been first available in 2005.)

The Berkeley Lab multiband semiconductor material was marketed and licensed in 2005.

## **6 Inventor or Principal Developer (List all developers from all companies)**

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## **7 Product price**

To be determined by the licensee.

## **8 Do you hold any patents or patents pending on this product?**

Yes. A patent application for “Multi-Band Semiconductors for High-Efficiency Solar Cells” has been filed with the United States Patent and Trademark Office and under the Patent Cooperation Treaty.

## **9 Describe your product’s primary function as clearly as possible. What does it do? How does it do it? What theories, if any, are involved?**

A seemingly unavoidable tradeoff between cost and power efficiency has, historically, relegated the solar cell to niche markets such as space power, military applications, and relatively low-cost, low-efficiency uses such as off-grid power. With its combination of low cost and full-spectrum efficiency, the Berkeley Lab multiband semiconductor demonstrates that this tradeoff is not inevitable, and opens a path forward for the development of photovoltaic systems as a major source of electric power.

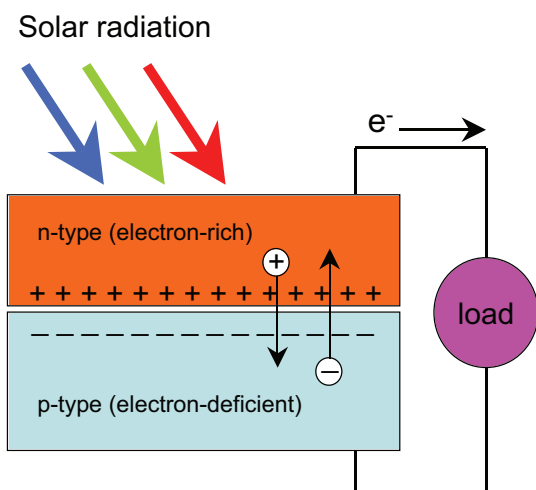
Every hour, enough solar energy reaches the earth's surface to fuel the world's energy needs for a full year. Just twenty days of sunshine contains energy equivalent to the earth's total fossil fuel reserves. Ever since their invention in the 1950's, semiconductor-based solar cells have held the promise of someday replacing fossil fuels and nuclear power with clean, environmentally friendly power. As the world faces an inevitable decline in fossil fuel reserves as well as global warming, tapping the limitless reserves of solar power becomes increasingly important. Now, with the invention of the multiband semiconductor, it has become feasible as well.

Despite the need for solar power, decades of research, and generous subsidies for installing photovoltaic systems, the contribution of photovoltaics to the global energy supply is miniscule. The reason is simple: because of their high manufacturing cost and limited efficiency, today's photovoltaic systems cannot compete with conventional electrical generation in most situations. Currently, the average retail customer in the US pays roughly 7.5 cents per kilowatt-hour for electricity. Residential solar power, using commercially available crystalline silicon modules, costs about five times more, about 35 cents per kWh.

In answer to the need for a highly efficient, affordable photovoltaic device, Berkeley Lab researchers Wladek Walukiewicz and Kin Man Yu have invented an entirely new type of semiconductor material, the highly mismatched alloy (HMA). HMA semiconductors are ideally suited for use in a new type of highly efficient, easy to manufacture solar cell: the multiband solar cell (MBSC). **Now licensed to a commercial partner, RoseStreet Labs, of Phoenix, AZ, the Berkeley Lab technology will be used to develop MBSCs that are capable of achieving extremely high power conversion efficiencies—up to a maximum limit of 63% for the available three-band HMA and, with further development, up to 72 % for a four-band HMA system—at a cost that is competitive with conventional electrical power sources.** This innovation represents a fundamental breakthrough in the properties of semiconductors used in solar cells.

### How Solar Cells Work

Figure 1 describes the basic operation of a solar cell. Conventional solar cells consist of a sandwich of an electron-rich, negatively charged n-type semiconductor and an electron-deficient, positively charged p-type semiconductor. The interface of the two semiconductors is called the junction. Most solar cells are single junction. A conventional solar cell has two energy states that electrons may occupy: a valence band that is fully populated with electrons, and a higher-energy conduction band that has empty states for electrons to occupy when they have absorbed energy from



**Figure 1** Electrons from the n-type semiconductor are attracted to the electron-deficient *p* side, and positively charged “holes” are attracted to the *n* side. When a quantity of electrons and holes have moved to their attracting sides, an electric field at the junction prevents further movement, only permitting movement of electrons to the *n* side and holes to the *p* side. Solar radiation frees up additional electrons and holes, greatly increasing the number of electrons on the *n* side and holes on the *p* side. A circuit provides a path around the junction, allowing electrons to flow to the *p* side, doing work along the way.

sunlight. These bands should be thought of as energy states of the electrons, not physical features of the semiconductor. Electrons in the valence band are bound closely to atoms in the semiconductor’s crystal matrix, but the energized electrons in the conduction band are free to move as an electric current through a circuit, translating solar radiation to electricity.

### The Band Gap and Solar Cell Efficiency

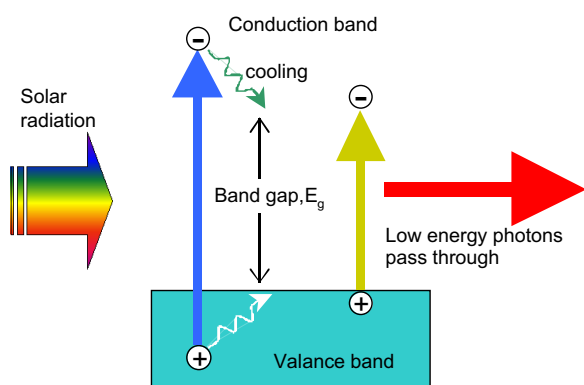
The *band gap* is the difference in energy between the valence band and the conduction band. In other words, it is equal to the amount of energy needed to promote an electron from the valence band to the conduction band. The band gap is crucial to the efficiency of a solar cell because the semiconductor only absorbs the part of the solar spectrum whose energy is equal to or greater than the band gap. Lower energy (longer wavelength) light passes through the semiconductor with no interaction taking place, and no electrons move. Light with energy higher (or wavelength shorter) than the band gap energy is absorbed, but the excess energy (i.e., photon energy minus the band gap energy) is also largely wasted, since the electrons, although moving to the conduction band, give up their excess energy as heat rather than electric power (Figure 3). These losses limit the power conversion efficiency of conventional, commercially available, silicon solar cells to around 15 percent, with a maximum theoretical limit of 40.7 percent.



**Figure 2** Photomodulated reflectance setup for measuring the band gap of multiband semiconductor materials.

The possibility of improving solar cell efficiency by using a semiconductor material with multiple band gaps, each corresponding to a different wavelength of light, was first proposed in 1960, but creating such a material has not been done until now. In the absence of a multiband material, researchers developed the multijunction solar cell, which achieves full-spectrum response by creating a stack of semiconductors of different bandwidths. However, multijunction solar cells, which can have 16 or more layers of semiconductors, are difficult and expensive to fabricate, and suffer efficiency losses through mismatching of the various layers' crystal lattices.

**Development of a single-junction multiband solar cell has only become possible with Berkeley Lab's breakthrough discovery and fabrication of the highly mismatched alloy (HMA), the world's first and only multiband semiconductor material.** A multiband solar cell (MBSC) using an HMA with three bands has a maximum theoretical efficiency of 63 percent, much greater than the 40.7 percent theoretical efficiency limit for silicon solar cells and over four times greater than the 15 percent typical of high-quality silicon cells now on the market. Using the band



**Figure 3** In a conventional, single junction solar cell, sunlight must be of an energy (i.e., frequency) greater than the band gap in order to promote electrons from the valence band to the conduction band. Photons with less energy pass through the semiconductor without transferring their energy. Electrons that have more than enough energy to cross the band gap release the excess energy as heat.

anticrossing theory of HMAs developed by the Berkeley Lab team, MBSCs using a four-band HMA with a maximum theoretical efficiency of 72 percent can also be realized. The beauty of the MBSC is that it achieves such a high efficiency in a cell similar in simplicity and structure to solar cells now on the market, an advantage that should enable it to be manufactured using existing processes and equipment.

**The combination of high efficiency and low manufacturing cost promises to make the MBSC competitive with fossil fuel and nuclear-based power.**

### The Highly Mismatched Alloy (HMA)

Invented by the Berkeley Lab research team, the highly mismatched alloy (HMA) is what makes the multiband solar cell possible. An entirely new type of semiconductor material, the HMA is unique in possessing more than one band gap. An HMA



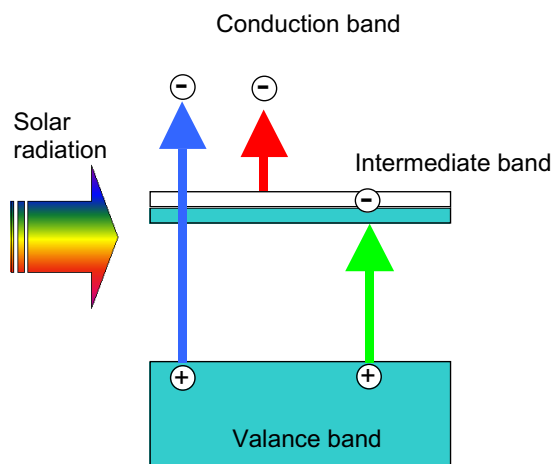


**Figure 4** Dr. Kin Man Yu at the controls of the Varian kVion implanter, used to implant dopant atoms of oxygen and nitrogen in the ZnMnTe and GaAsP semiconductor.

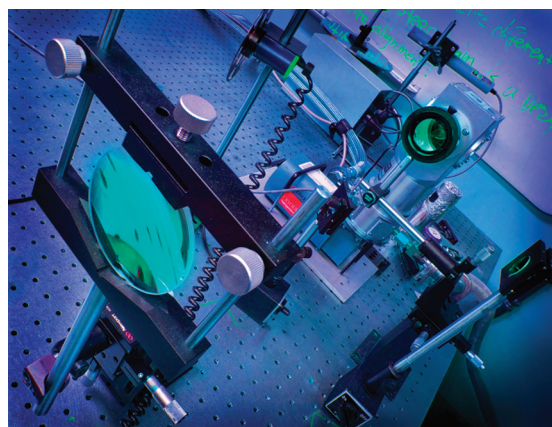
semiconductor is created when a small percentage of host atoms in a semiconductor is replaced with isovalent atoms of a very different size and electronegativity (dopant atoms). Alloying the semiconductor with these mismatched atoms—for example, replacing arsenic or phosphorus atoms with nitrogen in gallium arsenide phosphide (GaAsP) or some tellurium atoms with oxygen in zinc manganese telluride (ZnMnTe)—causes a radical change in the material’s electronic and optical properties: the energy level

induced by the mismatched atoms splits the semiconductor’s single conduction band into two separate bands. This phenomenon results from a quantum mechanical effect known as band anticrossing (BAC) and was first discovered and modeled by the Berkeley Lab team. The result is the first-ever semiconductor with three bands: a valence band, a conduction band, and between these two, an *intermediate band*.

The addition of an intermediate band is of great significance, because it allows light to be efficiently absorbed at three different energies, as explained in Figure 5.



**Figure 5** Multiband Solar Cell. The intermediate band acts as a “stepping stone,” allowing absorption of photons at three different energy levels, corresponding to the three different band gaps. In particular, low-energy photons are captured that would pass through a conventional solar cell.

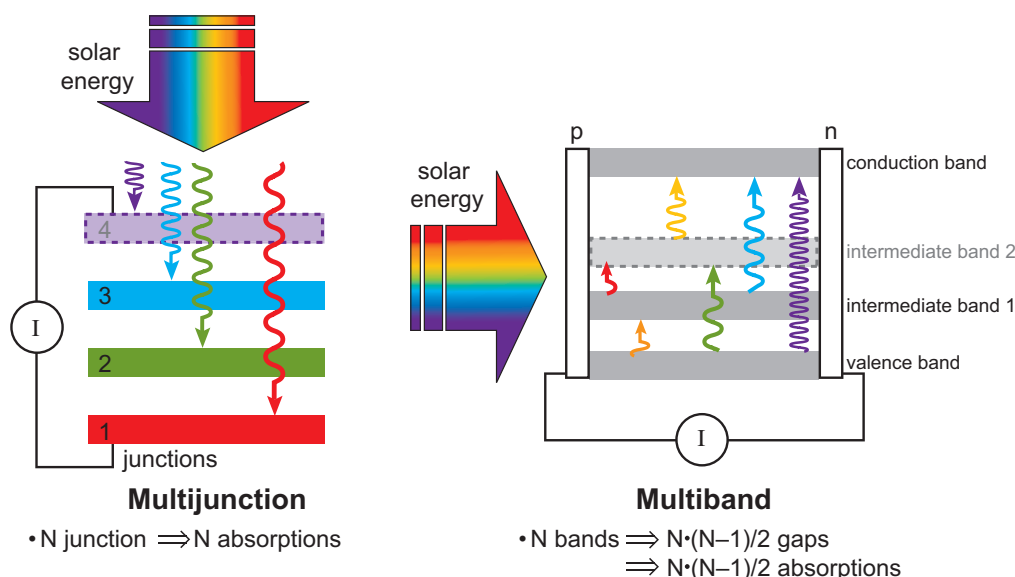


**Figure 6** Photoluminescent setup to measure the optical and photovoltaic effects of novel solar cell materials.

Every other known semiconductor can only absorb light efficiently at one energy. In addition, these band gaps can be adjusted by varying the proportions of alloy elements, making it possible to optimize the HMA to capture energy from the full spectrum of sunlight—from infrared to visible light to ultraviolet. It is also possible, by a similar method, to introduce a second intermediate band, providing even higher efficiency.

### The Multiband Solar Cell

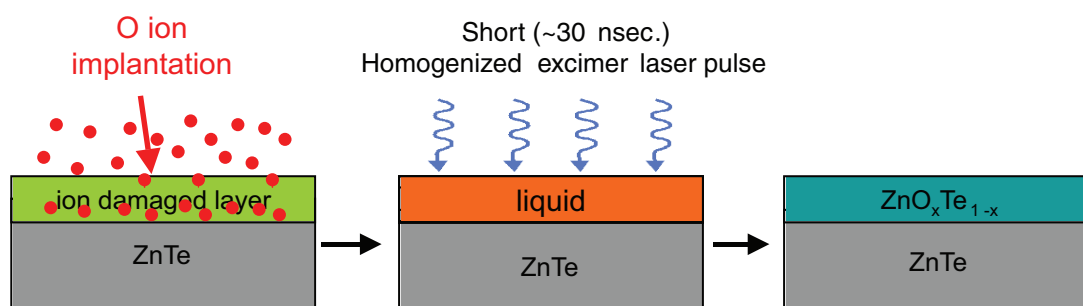
A multiband solar cell (MBSC) manufactured from our HMA multiband semiconductor material physically resembles a conventional single junction solar cell. However, in terms of its electronic properties it is crucially different. The semiconductor's additional intermediate band (or bands) forms an intermediate-energy “stepping stone” between the valence band and conduction band. As illustrated in Figure 5, the intermediate band allows lower-energy photons to promote electrons to the conduction band in steps rather than in one leap. Most importantly, the intermediate band creates two additional band gaps, allowing absorption of photons at three energies rather than one (See Figure 7). With further development a second intermediate band could be added to create three additional band gaps, providing a total of six absorption energies. Its unique property of supporting multiple band gaps allows the MBSC to efficiently convert light to electricity across the full solar spectrum.



**Figure 7** Adding intermediate bands to a multiband semiconductor adds a disproportionately large number of absorption energies (see equation above). By contrast, adding a junction to a multijunction solar cell adds only one absorption energy.

### Fabricating Highly Mismatched Alloys (HMAs)

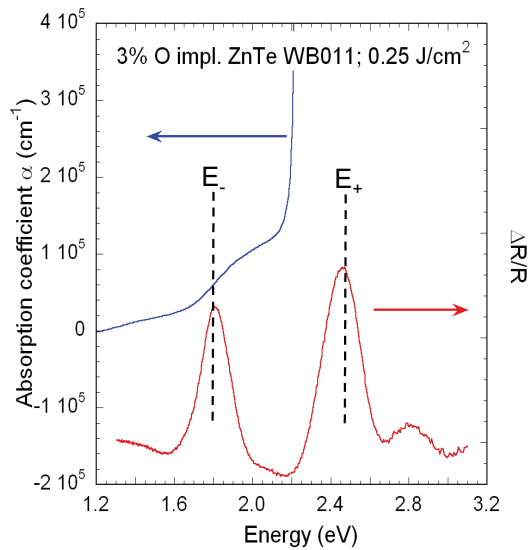
In addition to developing the band anticrossing (BAC) model, which accurately predicted the multiband phenomenon, Berkeley Lab has also devised and successfully applied a technique for fabricating HMA semiconductors. In HMAs, the impurity atoms (dopants) and host atoms are unwilling neighbors, and the dopants have a tendency to escape from the crystal matrix. To trap enough oxygen atoms in ZnMnTe or nitrogen atoms in GaAsP requires high-energy implantation, which damages the semiconductor crystal. If, when repairing the damage, the material is heated too slowly, the dopants are rapidly driven out. Berkeley Lab uses pulsed laser melting (PLM) in short excimer laser pulses, typically 30 nsec in duration, to melt and rapidly recrystallize the damaged layer before the oxygen or nitrogen can escape (see Figure 8).



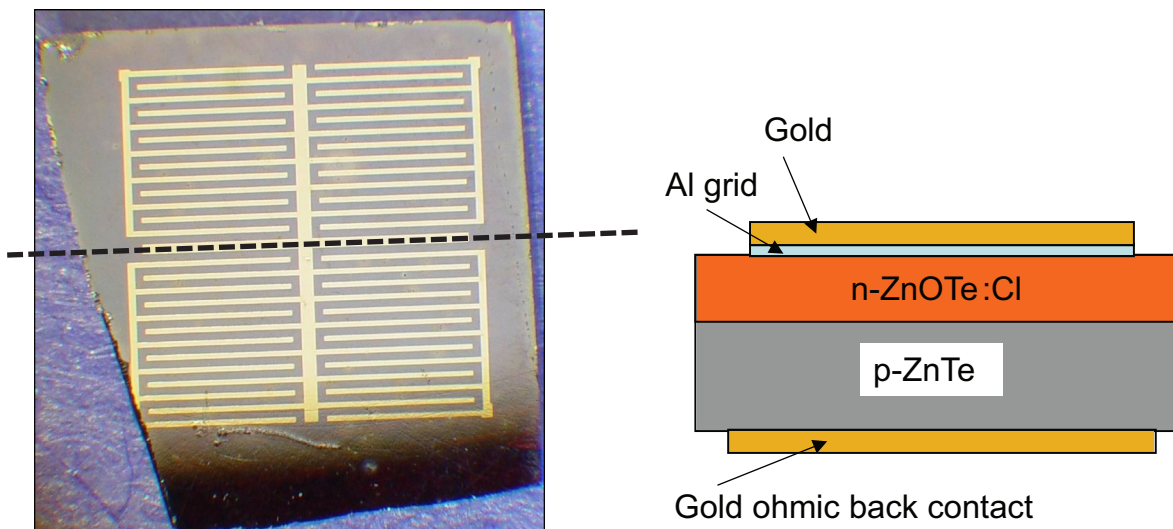
**Figure 8** Pulsed Laser Melting. O or N (up to 5 percent) is introduced into the ZnMnTe or GaAsP matrix, respectively, by ion implantation (left). A 30 nsec excimer laser pulse is used to rapidly melt and regrow the layer (~0.2-0.5mm) damaged by ion implantation (middle). This process traps the O or N in the lattice site (right).

Proof of the successful synthesis of an intermediate band semiconductor is demonstrated in Figure 9, which shows optical spectra of oxygen-doped zinc manganese telluride, ZnMnOTe. Two transitions, to the intermediate band E<sup>-</sup> and to the upper conduction band E<sup>+</sup>, are clearly observed. Large absorption coefficients for the transitions to the intermediate band indicate that most of the light will be absorbed in thin films produced by PLM. Figure 10 is a photograph of a prototype solar cell fabricated by this process.





**Figure 9** Optical Spectra of ZnMnOTe. Peaks at E- and E+ indicate light absorption as electrons transition to the intermediate band and conduction band.



**Figure 10** Prototype multiband solar cell. Left: a top-view photograph of a Cl doped n-ZnOTe layer (~0.2mm thick) synthesized by O+Cl ion implantation followed by pulsed laser melting. The grid structure is an Al/Au ohmic contact on the ZnOTe. The substrate is p-type ZnTe. Right: a cross-sectional schematic of the device.

**10A List your product's competitors by manufacturer, brand name and model number.**

- SunPower A-300 monocrystalline silicon solar cell
- Sharp NT-S5E1U monocrystalline silicon photovoltaic module
- Shell Solar PowerMax Eclipse copper indium diselenide thin film
- Sanyo HIT190 monocrystalline/amorphous silicon solar cell
- Kyocera SPG200T-02 multicrystal silicon solar module
- Spectrolab Ultra Triple Junction (UTJ) multijunction solar cell
- Emcore Advanced Triple Junction (ATJ) multijunction solar cell

## COMPETITIVE MATRIX

10B Supply a matrix or table showing how the key features of your product compare to existing products or technologies. Include both numerical and descriptive comparisons.

	Berkeley Lab Multiband Semiconductor Material (ZnMnOTe) or (GaNASP)	Silicon Semiconductor (SunPower, Sharp, Sanyo, Kyocera)	Thin Film Semiconductor (Shell Solar) (Si, copper indi- um gallium dise- lenide (CIGS), CdTe) (ISET)	Multijunction (3-junction) Semiconductor System (Spectrolab, Emcore.) GaInP2/GaAs/Ge	LBNL/Cornell InGaN full spectrum Multijunction Semiconductor System	Competitive Advantage of Berkeley Lab Multiband Semiconductor Material
Cost per kWh (20- year life span)	\$.075 - \$.10	\$.35	\$0.25	Very high (>\$100)	high	Expected to be com- petitive with fossil fuel/ nuclear power.
Power conversion efficiency limit (maximum concen- trated sunlight)	63% (one intermediate band)  72% (two intermediate bands)	40.7%	40.7%	55.8, 63.8, 72% (2,3, or 5 junctions)	55.8, 63.8, 72% (2,3, or 5 junctions)	50% to 76% more energy than silicon or thin film cells. Efficiency higher than or equal to complex multijunc- tion cells
Flexibility (ability to select band gaps to optimize perform- ance)	Very flexible	Not flexible	Not flexible	Some flexibility (by selecting differ- ent materials)	Flexible by composition tuning	Tunability of the band gaps (by adjusting composi- tion) results in near perfect match to the solar spectrum
Radiation resistance (hardness)	Medium	Very low	Medium for copper indium gallium dise- lenide (CIGS)	Low (complex structures sensitive)	Very high	Suitable for space applications where low cost is an advantage.

	<b>Berkeley Lab Multiband Semiconductor Material (ZnMnOTe) or (GaNASP)</b>	<b>Silicon Semiconductor (SunPower , Sharp, Sanyo, Kyocera)</b>	<b>Thin Film Semiconductor (Shell Solar) (Si, copper indi- um gallium dise- lenide (CIGS), CdTe) (ISET)</b>	<b>Multijunction (3-junction) Semiconductor System (Spectrolab, Emcore,) GaInP2/GaAs/Ge</b>	<b>LBNL/Cornell InGaN full spectrum Multijunction Semiconductor System</b>	<b>Competitive Advantage of Berkeley Lab Multiband Semiconductor Material</b>
Sensitivity to struc- tural imperfections	Low	High	Medium	High	Very low	Suitable for harsh environments such as space. Permits less strict greater manufacturing toler- ances.
Ease of fabrication	Simple single-junc- tion device	Simple single-junc- tion device	Simple single-junc- tion device	Complex design involving the growth and matching of many layers of dif- ferent materials	Requires growth of many layers with different alloy com- position and match- ing of these layers	Simple single-junc- tion cells are far eas- ier and faster to manufacture
Compatibility with existing manufactur- ing processes	Compatible with existing mass pro- duction techniques	Compatible	Compatible	Incompatible: complex design requires more com- plex manufacturing process	Incompatible: complex design requires more com- plex manufacturing process	Relatively low man- ufacturing cost will allow MBSC to pro- duce cost competi- tive electricity

## 10C Describe how your product improves upon competitive products or technologies.

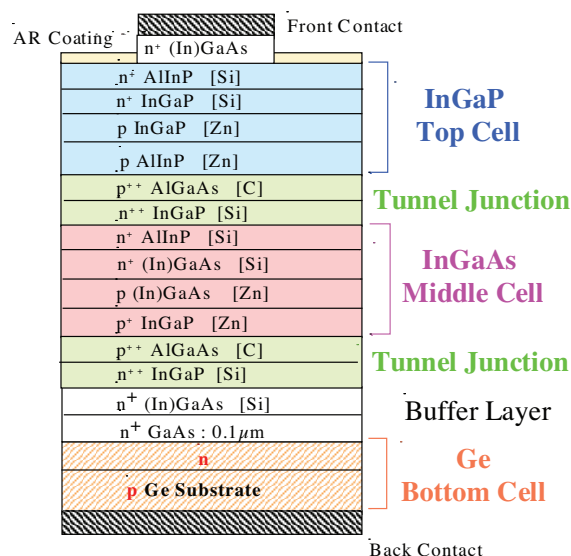
The multiband semiconductor makes possible the multiband solar cell (MBSC), which is unique in possessing the combination of low cost and high efficiency needed to enable photovoltaic systems, to produce electricity that is cost-competitive with fossil fuel generation. The MSBC provides the following advantages over other solar cell technologies:

**Highly efficient conversion of solar energy to electricity:** A three-band MBSC has a maximum calculated power conversion efficiency, in maximum concentrated sunlight, of 63 percent, increasing to 72 percent for a four-band cell. This is comparable to multijunction cells consisting of three and five junctions, respectively, and much greater than the theoretical limit of 40.7 percent for both conventional silicon and thin-film technologies. At present, the best commercial, real-world efficiency for a silicon solar cell is 15 percent.

**Low cost per installed watt:** Because they are single-junction semiconductors, MBSCs are relatively easy to fabricate. In addition, they are substantially more efficient than other single-junction solar cells, so their cost per installed watt is substantially lower. Multijunction cells are also highly efficient, but their designs are far more complex. A three-junction cell requires six different elements, three different dopants and 16 layers in all. (see Figure 11).

The cost of fabricating multijunction solar cells is on the order of 100 times more than MBSCs, making them prohibitively expensive. MBSCs are expected to be

**Figure 11** An advanced three-junction multijunction solar cell has multiple layers of different semiconductor materials. Although efficient, it's complexity and the problem of lattice mismatching between layers makes it prohibitively expensive for general power generation.



M. Yamaguchi *et. al.* – Space Power Workshop 2003



comparable to silicon and thin-film technologies in terms of fabrication cost, while outperforming them in power conversion efficiency.

**Compatible with today's manufacturing processes:** The MBSC is expected to be compatible with existing mass-manufacturing techniques, an advantage that would allow it to enter high-volume production quickly and to take advantage of existing economies of scale. No other advanced solar cell has the ability to “plug in” to an existing manufacturing base.

**Easily optimized:** The separation of the various bands in an MBSC can be adjusted by altering the percentage of alloy elements; for example, the proportion of Mn in ZnMnOTe can be varied from 0 to 15 percent so that a near-perfect match to the solar spectrum is possible.

**High fault tolerance:** An important factor in both cost and service lifetime is the semiconductor's sensitivity to structural imperfections in the crystal lattice. Crystalline silicon and multijunction solar cells have a high sensitivity to structural flaws, while thin-film cells are moderately sensitive. Imperfections in the crystal lattice occur during fabrication and in the field as a result of solar radiation damage, and can reduce the efficiency of current solar arrays by 20 percent over 20 years. The multiband solar cell material is very tolerant of faults, whether introduced during fabrication or through usage as the result of radiation damage. Its fault tolerance will make manufacturing quality control simpler and less expensive than for current silicon cells. Its good radiation hardness also makes the MBSC suitable for harsh environments such as space. Although some solar cells, namely the LBNL/Cornell multijunction cell, have superior radiation hardness, the low cost of the MBSC compensates for this difference in many applications.

#### **11A Describe the principal applications of this product.**

The multiband solar cell's primary application is to produce electric power for residential, commercial, government, and military applications. Its combination of low cost and high power conversion efficiency will make it cost competitive with, or less expensive than, fossil fuel power.

#### **11B List all other applications for which your product can now be used.**

Solar cells on satellites—Multiband semiconductors have good radiation hardness. Combined with their low cost and high power density, this makes them competitive with higher cost multijunction solar cells for many space applications.

Sensors – The efficiency and tunability of MBSCs make them an attractive choice as photodiodes for detection of optical communications signals.

Off-grid solar applications, military, appliances, portable devices.

**12 Summary. State in layman's terms why you feel your product should receive an R&D 100 Award. Why is it important to have this product? What benefits will it provide?**

Today, a typical residential photovoltaic system has a power conversion efficiency of about 15 percent, with a theoretical limit of 40.7 percent. Three-band MBSC's theoretical maximum efficiency of 63 percent (72 percent for four-band MBSC's) is over four times (almost five times) greater than the current standard. Since solar power is currently five times more costly than grid power, such an increase in efficiency would achieve the goal of making solar power cost-competitive with grid power, reducing its cost from today's approximately 35cents per kilowatt-hour to around 75 cents per kWh, which is the national average for conventional grid power.

Among the many emerging photovoltaic technologies, only multiband solar cells provide the combination of low cost and high efficiency that is necessary if solar power is to finally fulfill its promise of producing inexpensive, widely available, carbon neutral energy. In a world facing declining fossil fuel reserves and already feeling the effects of global warming, the fulfillment of this promise could be decisive.

## ORGANIZATION DATA

### 13 Contact person to handle all arrangements on exhibits, banquet, and publicity.

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**Appendix**  
**List of Attachments**  
**2005 R&D 100 AWARDS**  
**ENTRY— High Efficiency Multiband Semiconductor**  
**Material for Solar Cells**

**A. Letters of Support**

- The European Space Agency
- Instituto de Energia Solar
- Ritsumeikan University
- RoseStreet Labs
- University of California, San Diego

**B. Selected Press Coverage**

- “Commentary: Super-efficient solar cells in prospect,” United Press International, November 11, 2003 (attached).
- “Photovoltaic Cells:Power at a Price,” Chemical & Engineering News, June 21, 2004 (attached).
- “Multi-Bandgap Semiconducting Materials Boost Solar-Cell Efficiency,” MRS Bulletin, August, 2005 (attached).
- “Catching More Rays,” Biological Research Information Center, November 10, 2003 (attached).
- “Boosting Solar Cell Efficiency,” The Washington Post, November 25, 2003
- “Novel Semiconductor Could Soup Up Solar Cells,” Scientific American, November 10, 2003 (attached).

**C. Publications**

- “Diluted II-VI Oxide Semiconductors with Multiple Band Gaps,” K. M. Yu, W. Walukiewicz, J. Wu, W. Shan, J.W. Beeman, Lawrence Berkeley National Laboratory; M.A. Scarpulla, O.D. Dubon, Lawrence Berkeley National Laboratory/University of California, Berkeley; P. Becla, Massachusetts Institute of Technology. December 12, 2003, Physical Review Letters, Vol 91, No.24, The American Physical Society (attached).
- “Highly Mismatched Alloys for Intermediate Band Solar Cells,” W. Walukiewicz, K. M. Yu, Lawrence Berkeley National Laboratory; J. Wu,

Harvard University; J.W. Ager III, W. Shan, Lawrence Berkeley National Laboratory; M.A. Scarpulla, O.D. Dubon, Lawrence Berkeley National Laboratory/University of California, Berkeley; P. Becla, Massachusetts Institute of Technology. Materials Research Society Symposium Proceedings, Vol 865, Materials Research Society, 2005 (attached).

- “Synthesis and optical properties of II-O-VI highly mismatched alloys,” K. M. Yu, W. Walukiewicz, W. Shan, J. Wu, J.W. Beeman, Lawrence Berkeley National Laboratory. Journal of Applied Physics, Vol 95, No. 11, June 1, 2004, American Institute of Physics, 2004 (attached).



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**Appendix A:**

**Letters of Support**

**2005 R&D 100 AWARDS**  
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**Appendix B:**

**Selected Press Coverage**

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**Appendix C:**

**Publications**